Adsorption Integral Equation via Complex Approximation with Constraints: The Langmuir Kernel

VLADIMIR A. BUSHENKOV,[1] J. P. PRATES RAMALHO,[2] GEORGI V. SMIRNOV[3]

[1]*Departamento de Matemática, Universidade de Évora apartado 94, 7000 Évora, Portugal*
[2]*Departamento de Quimica, Universidade de Évora apartado 94, 7000 Évora, Portugal*
[3]*Centro de Matemática Aplicada, Departamento de Matemática Aplicada, Faculdade de Ciências Universidade do Porto, Rua das Taipas 135, 4050 Porto, Portugal*

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ABSTRACT: The relationship between the measured adsorption isotherm and unknown energy distribution function is described by so-called adsorption integral equation, a linear Fredholm integral equation of the first kind. We consider the case of the Langmuir kernel when the equation can be reduced to the Stieltjes integral equation. A new method for solving the Stieltjes equation is developed. The method is based on the ideas of complex approximation with constraints. The numerical algorithms constructed on the base of this method allow reduction of the problem under consideration to linear or linear-quadratic programming problems. The method is compared with the usual regularization methods. The obtained results can be useful for the evaluation of the experimental adsorption energy distribution from experimental data. J Comput Chem 21: 191–200, 2000

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Introduction

Any adequate theory of adsorption on real surfaces must take into account the surface heterogeneity in adsorption energy. The main source of this surface heterogeneity arises from the existence of local crystalline disorder, presence of impurities strongly bonded with the surface, surface roughness, etc.

It is usually assumed that the heterogeneous adsorbents are characterized by continuous distribution of adsorption energy, instead of a single adsorption energy value that could characterize an ideal homogeneous surface. The relationship between the measured adsorption isotherm and the unknown energy distribution function is described

Correspondence to: J. P. Prates Ramalho; e-mail: jpcar@dquim.uevora.pt

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by the adsorption integral equation

$$\theta(p) = \int_0^\infty \theta(p, E) N(E)\, dE, \qquad (1)$$

where p is the equilibrium pressure, E is the adsorption energy, $\theta(p, E)$ is a local adsorption isotherm, $\theta(p)$ is a global adsorption isotherm that is experimentally measured, and $N(E)$ is a relative number of adsorbing centers with the energy E. The function N is defined for nonnegative values of E, takes nonnegative values, and satisfies the condition

$$\int_0^\infty N(E)\, dE = 1. \qquad (2)$$

The local adsorption isotherm, $\theta(p, E)$, is the kernel of the integral equation, and represents the accepted model of adsorption. It describes adsorption on an homogeneous surface with adsorption energy E, and makes the bridge between ideal homogeneous surface and real heterogeneous adsorbents.

From a mathematical point of view, to find the energy distribution function amounts to solving a Fredholm equation of fist kind. This problem is known as ill-posed. The difficulty in solving the equation arises from the fact that small variations in the total isotherm $\theta(p)$ may lead to large changes in the distribution function. This problem is more dramatic, because $\theta(p)$ is usually only known as a discrete set of experimental values in a limited range of pressures, moreover, with inevitable experimental errors.

An extensive review of methods to solve this equation in adsorption context has been presented by Jaroniec and Madey.[1] According to Re,[2] three general classes of methods have been used to solve eq. (1): (1) *analytical methods* first introduced by Sips[3,4] and developed later by Misra,[5–7] based on integral transform theory and in which both the local and the global isotherms have an explicit analytical form; (2) *numerical methods*, which can be simple as an elementary optimization of a parameterized form or more accurate methods, which take into account the ill-posed character of the Fredholm equation of first kind. Examples of these methods are the singular value decomposition (SDV),[8,9] regularization,[10–14] combination of regularization principle with the B-spline representation of the distribution function,[15] and CAEDMON[16,17]; (3) *approximate methods* based on approximations imposed on the local isotherm.[18–26] The most popular and commonly used approximation method is the condensation approximation.[18]

There are also hybrid methods like the method proposed by Villiéras et al.[27] that is a hybrid between analytical and approximate methods. The methods can also be classified as local and global.[28] The global methods give the distribution function in the whole domain of energies and require the knowledge of the experimental global isotherm in the complete range of pressures, that means, for $p \in (0, +\infty)$. The local methods give the distribution function in a limited range of adsorption energies and require the knowledge of the global isotherm in a limited pressures domain. Usually, the approximate methods are of local character.

Recently, it has been shown that for monolayer adsorption on a surface, including arbitrary range lateral interactions, the isotherm can be written as a power series of the Langmuir isotherm.[29] If a truncated series isotherm or the complete series isotherm is used as kernel for the adsorption integral equation, it can be transformed into an integral equation with the Langmuir kernel with a modified global isotherm.[29] It has been shown elsewhere also that the local Langmuir isotherm can be modified to account for lateral interactions.[21,30] On the other hand, it is well known that in the case of the Langmuir kernel the adsorption integral equation can be transformed into the Stieltjes integral equation (see Sips[3,4]). Thus, for rather general cases, the adsorption integral equation reduces to a Stieltjes integral equation, which has an analytical solution.

The fact that there exists a formula for the solution to the integral equation does not mean that the problem is completely solved. Because the global isotherm is usually known as a discrete set of experimental values in a limited range of pressures, the use of numerical methods is inevitable.

In this work a new method for solving the Stieltjes equation is developed. The method presented here is based on the ideas of complex approximation with constraints.[43] In chemical experiments the global isotherm θ is known only at some points $p_l > 0$, $l = 1, 2, \ldots, L$. It was shown[43] that if $L \to \infty$, this information is enough to reconstruct the function $\theta(p)$, $p > 0$. We reduce the reconstruction of $\theta(p)$, and thus the solution of the Stieltjes equation to a problem of complex analytic continuation with prescribed bound. This problem was largely studied (see refs. 32–39, for example). The method presented in this article is closed in spirit to the mentioned works. The main feature of our approach is the use of eq. (2) to derive the bounds for the Taylor coefficient of the analytic function to be found. The numerical algorithms constructed on the base of this method allow reduction of the problem under

consideration to linear or linear-quadratic programming problems. The obtained results can be useful for the evaluation of the experimental adsorption energy distribution from experimental data.

This article is organized as follows. In the first section, following Sips,[3, 4] we reduce the adsorption integral equation with the Langmuir kernel to the Stieltjes integral equation. Some useful properties of this equation are established in the second section. The third section is devoted to approximation with constraints. In the fourth section we describe the numerical algorithms. The fifth section contains some results of numerical experiments. Finally, in the last section, we present a conclusion and perspectives of future work.

The Adsorption Integral Equation and the Stieltjes Integral Equation

As we have seen before, the relationship between the measured adsorption isotherm and the unknown energy distribution function is given by

$$\theta(p) = \int_0^\infty \theta(p, E) N(E)\, dE. \tag{3}$$

Being a distribution function, N is defined for nonnegative values of E, takes nonnegative values, and satisfies the condition

$$\int_0^\infty N(E)\, dE = 1. \tag{4}$$

Under rather general conditions[29, 40] the local isotherm depends on the product $K(E)p$:

$$\theta(p, E) = \Theta\big(K(E)p\big), \tag{5}$$

where $K(E) = K_0 \exp(E/K_B T)$, T is a temperature, K_B is the Bolzmann constant, and K_0 is a constant.[1] Introducing the variable $K = K(E)$, from eqs. (3) and (2) we get

$$\theta(p) = \int_0^\infty \Theta(Kp) \mathcal{N}(K)\, dK \tag{6}$$

and

$$\int_0^\infty \mathcal{N}(K)\, dK = 1, \tag{7}$$

respectively, where

$$\mathcal{N}(K) = \begin{cases} 0, & K \in [0, K_0], \\ (K_B T/K) N(E(K)), & K \in (K_0, +\infty). \end{cases} \tag{8}$$

We assume that the function $\Theta = \Theta(s)$ has the form

$$\Theta(Kp) = \frac{Kp}{1 + Kp}.$$

This form of local isotherm was introduced by Langmuir, and is largely used in the adsorption theory. Originally introduced as a kernel accepting the model of monolayer adsorption neglecting interactions between adsorbed molecules, it was shown that more complicate problems, including nonidealities, can also be reduced to an integral equation with Langmuir kernel.[29] In this case, eq. (6) can be reduced to the Stieltjes integral equation. Indeed, put $t = K$, $\xi = 1/p$, $\phi(t) = t\mathcal{N}(t)$, and $\Phi(\xi) = \theta(1/\xi)$. Then from eq. (6) we have

$$\Phi(\xi) = \int_0^\infty \frac{\phi(t)\, dt}{t + \xi}, \tag{9}$$

where $\Phi(\xi)$, $\xi \geq 1$, is a known function and the problem is to find $\phi(t) \geq 0$, $t \in [0, \infty)$. Moreover ϕ satisfies

$$\int_0^\infty \frac{\phi(t)\, dt}{t} = 1. \tag{10}$$

For the sake of simplicity, we shall consider this problem in the class of continuous functions ϕ. From eq. (9) it follows that $\Phi(\xi)$ is analytic in the complex plane cut along the ray $L = \{\xi \mid \operatorname{Re}\xi \leq 0,\ \operatorname{Im}\xi = 0\}$, and

$$\phi(x) = \lim_{y \downarrow 0} \frac{\Phi(-x - iy) - \Phi(-x + iy)}{2\pi i}, \qquad x > 0, \tag{11}$$

(see ref. 41). This solution to eq. (9) was obtained by Stieltjes, and it was used by Sips[3, 4] to the energy distribution function for some empirical isotherm equations. He assumed the global isotherm $\theta(p)$, or equivalently, function $\Phi(\xi)$ to be known in the complex plane cut along the negative real ray. As the global isotherm θ is experimentally obtained, we assume that it is known only at a sequence of points $p_l > 0$, $l = 1, 2, \ldots$. As it will be clear from our consideration this information is enough to reconstruct the function $\theta(p)$ in the complex plane cut along the negative real ray. We reduce the function θ reconstruction problem and, therefore, the solution of the Stieltjes equation to a problem of complex analytic continuation with prescribed bound. The main feature of the approach presented here is the use of eq. (7) to derive bounds for the Taylor coefficient of the analytic function under consideration. This allows reduction of the analytic continuation problem to a sequence of mathematical programming problems.

Some Properties of the Stieltjes Integral Equation

Consider the conformal mapping

$$w = \frac{\sqrt{p}-1}{\sqrt{p}+1}, \tag{12}$$

where by $\sqrt{p}$ we mean the branch satisfying $\sqrt{1}=1$. It maps the plane cut along $L = \{p \mid \operatorname{Re} p \le 0, \operatorname{Im} p = 0\}$ onto the unit disk $K = \{w \mid |w| < 1\}$. The "upper" side of L, $L^+ = \{p + i0\}$, is transformed into the set $\Gamma^+ = \{w \mid |w| = 1,\ \operatorname{Im} w > 0\}$ and the "lower" side of L, $L^- = \{p - i0\}$, is mapped on the set $\Gamma^- = \{w \mid |w| = 1,\ \operatorname{Im} w < 0\}$. Finally, the image of the ray $-L$ is the disk's diameter, $(-1, 1)$. The inverse of $w = w(p)$ is given by

$$p = \left(\frac{1+w}{1-w}\right)^2. \tag{13}$$

In the complex plane w integral, eq. (9) has the form

$$\Psi(w) = -\int_{\Gamma^+} \mathcal{K}(w,\tau)\psi(\tau)\,d\tau, \qquad -1 < w < 1, \tag{14}$$

where

$$\Psi(w) = \Phi\left(\left(\frac{1-w}{1+w}\right)^2\right),$$
$$\psi(\tau) = \phi\left(-\left(\frac{1-\tau}{1+\tau}\right)^2\right),$$

and

$$\mathcal{K}(w,\tau) = \left(\frac{1+w}{1+\tau}\right)\left(\frac{1}{w-\tau} + \frac{1}{1-\tau w}\right).$$

If $|w| < 1$ and $|\tau| = 1$, we can represent $\mathcal{K}(w,\tau)$ in the following form

$$\mathcal{K}(w,\tau) = \left(\frac{1+w}{1+\tau}\right)\left(-\frac{1}{\tau}\left(1 + \frac{w}{\tau} + \frac{w^2}{\tau^2} + \cdots\right) + \left(1 + \tau w + \tau^2 w^2 + \cdots\right)\right).$$

Combining this with eq. (14), we obtain

$$\Psi(w) = -\int_{\Gamma^+} \frac{\tau - 1}{\tau(\tau+1)}\psi(\tau)\,d\tau - \sum_{k=1}^{\infty}\left(\int_{\Gamma^+}\left(\tau^{k-1} - \tau^{-k-1}\right)\psi(\tau)\,d\tau\right)w^k. \tag{15}$$

Putting $\tau = e^{i\nu}$, $\nu \in [0, \pi]$, from eq. (5) we get

$$\Psi(w) = \pi\sum_{k=0}^{\infty} b_k w^k, \tag{16}$$

where

$$b_0 = \frac{1}{\pi}\int_0^{\pi} \frac{1-\cos\nu}{2}\mathcal{N}\left(\frac{1-\cos\nu}{1+\cos\nu}\right)d\left(\frac{1-\cos\nu}{1+\cos\nu}\right)$$

and

$$\begin{aligned} b_k &= \frac{1}{\pi}\int_0^{\pi} \sin k\nu \sin\nu \mathcal{N}\left(\frac{1-\cos\nu}{1+\cos\nu}\right)d\left(\frac{1-\cos\nu}{1+\cos\nu}\right) \\ &= \frac{2}{\pi}\int_0^{\pi} \sin k\nu\left(\frac{1-\cos\nu}{1+\cos\nu}\right)\mathcal{N}\left(\frac{1-\cos\nu}{1+\cos\nu}\right)d\nu \\ &= \frac{2}{\pi}\int_0^{\pi} \sin k\nu\phi\left(\frac{1-\cos\nu}{1+\cos\nu}\right)d\nu, \qquad k = 1, 2, \ldots. \end{aligned}$$

The jump relation, eq. (11), can now be rewritten as

$$\psi(w) = \lim_{|w|\uparrow 1,\ \operatorname{Im} w > 0} \frac{\Psi(\overline{w}) - \Psi(w)}{2\pi i}. \tag{17}$$

Setting $w = \rho e^{i\mu}$, $\rho > 0$, $\mu \in (0, \pi)$, from eq. (16) we obtain

$$\varphi(\mu) = \phi\left(\frac{1-\cos\mu}{1+\cos\mu}\right) = -\lim_{\rho\uparrow 1}\sum_{k=1}^{\infty} b_k \rho^k \sin k\mu. \tag{18}$$

Thus, the function $-\varphi$ is a limit of the Abel means of its Fourier sine series (see ref. 42). Comparing eqs. (16) and (18), we see that the sine Fourier coefficients of $-\varphi$ are the Taylor coefficients of Ψ divided by π.

The approximation techniques presented below are based on the following estimates for the coefficients b_k, $k = 1, 2, \ldots$,

$$\begin{aligned} |b_k| &\le \frac{1}{\pi}\int_0^{\pi} \mathcal{N}\left(\frac{1-\cos\nu}{1+\cos\nu}\right)d\left(\frac{1-\cos\nu}{1+\cos\nu}\right) \\ &= \frac{1}{\pi}\int_0^{\infty} \mathcal{N}(K)\,dK = \frac{1}{\pi}, \qquad k = 1, 2, \ldots. \end{aligned} \tag{19}$$

Approximation with Constraints

From the previous consideration we see that the reconstruction of the function θ and solution of the Stieltjes equation can be reduced to the problem of complex analytic continuation of a function, analytic in the unit disk, with prescribed bounds for the Taylor coefficients. Here we present a method that allows obtaining an approximate solution to this problem, stable with respect to small perturbations of the data.

Consider a function f analytic in the unit disk $K = \{w \mid |w| < 1\}$. The function f can be written as

$$f(w) = \sum_{k=0}^{\infty} b_k w^k, \qquad |w| < 1.$$

We assume that

$$|b_k| \le d_k, \qquad k = 0, 1, 2, \ldots. \tag{20}$$

Let $\{z_k\}_{k=0}^{\infty}$ be a sequence of complex numbers. By $\vec{z}_n$ we shall denote the n-dimensional vector consisting of the first n terms of the sequence: $\vec{z}_n = (z_0, z_1, \ldots, z_{n-1})$. By $V_n^m(\vec{z}_n)$ we denote the m-norm in the n-dimensional space:

$$V_n^m(\vec{z}_n) = \left(\sum_{k=0}^{n-1} |z_k|^m \right)^{1/m}, \qquad m = 1, 2, \ldots,$$

and for $m = \infty$ we put

$$V_n^{\infty}(\vec{z}_n) = \max_{k=\overline{0,n-1}} |z_k|.$$

Let $\{B_k\}_{k=0}^{\infty}$ be a sequence of complex numbers. Define the polynomials

$$P(w, \vec{B}_n) = \sum_{k=0}^{n-1} B_k w^k.$$

Consider two sequences $\{w_k\}_{k=0}^{\infty}$ and $\{f_k\}_{k=0}^{\infty}$. We assume that $|w_k| \le r < 1$. Let $\bar{n}(n)$ be a sequence of nonnegative integers satisfying $\bar{n}(n) \ge n$, $n = 0, 1, \ldots$. Put

$$\vec{P}(\vec{B}_n) = \left(P(w_0, \vec{B}_n), P(w_1, \vec{B}_n), \ldots, P(w_{\bar{n}(n)-1}, \vec{B}_n)\right)$$

and

$$\vec{\tilde{f}}_n = \left(f(w_0), f(w_1), \ldots, f(w_{\bar{n}(n)-1})\right).$$

Here, the points w_k, $k = 0, 1, \ldots$, are the points where we know approximate values f_k, $k = 0, 1, \ldots$, of the function f. These values are, in general, different from the values $f(w_k)$, $k = 0, 1, \ldots$. Put $\vec{\hat{B}}_n = (b_0, b_1, \ldots, b_{n-1})$. Our aim is to find the coefficients b_k, $k = 0, 1, \ldots$. To this end we construct approximations of the function f by polynomials with coefficients satisfying restrictions in eq. (20).

Let m be a positive integer or ∞. Consider the following optimization problem

$$\text{minimize}\left\{V_{\bar{n}(n)}^m\left(\vec{P}(\vec{B}_n) - \vec{\tilde{f}}_{\bar{n}(n)}\right) \mid |B_k| \le d_k, \quad k = \overline{0, n-1}\right\}. \tag{21}$$

The solution to this problem we denote by $\vec{\hat{B}}_n = (\hat{B}_0, \hat{B}_1, \ldots, \hat{B}_{n-1})$.

Theorem 1. Assume that

1. $\lim_{n\to\infty} \sqrt[m]{\bar{n}(n)} \sum_{k=n+1}^{\infty} d_k \rho^k = 0, \forall \rho \in [0, 1)$,
2. $\lim_{n\to\infty} V_n^m(\vec{f}_n - \vec{\tilde{f}}_n) = 0$.

Then the polynomials $P(w, \vec{B}_n)$ converge uniformly inside the circle $K = \{w \mid |w| < 1\}$ to the function $f(w)$ as n goes to infinity.

The proof of this result can be found in ref. 43.

Let us discuss the role of restrictions in eq. (21). Note that without constraints in optimization problem (21) with $\bar{n}(n) = n$ the coordinates of the vector $\vec{B}_n$ are the coefficients of the usual Lagrange interpolation polynomial. If, for instance, the sequence w_l, $l = 0, 1, \ldots$, has only one limit point $w = 0$ and $\Psi_l = \Psi(w_l)$, $l = 0, 1, \ldots$, then the Lagrange interpolation polynomials also approximate the function inside the unit circle (see ref. 46). However, as it is well known, this approximation method is not stable with respect to small perturbations of the data Ψ_l, $l = 0, 1, \ldots$.

As a simple example, let us take $\Psi(w) = -i\epsilon \sin nw$ to model an "experimental" constant zero function measured at n points with an error $\pm\epsilon$. For this function, applying eq. (17), one obtains $\psi(i) = \Psi(i) - \Psi(-i) = \epsilon(e^n - e^{-n})$, which means that the error can grow exponentially with the number of experimental points. Thus, the bounds for the Taylor coefficients can be considered as a regularization. Note that the regularization effect of constraints in the analytic continuation problem and in the theory of the Fredholm equation of the first kind is well known (see refs. 36 and 37, for example).

This kind of regularization is the natural one for the problem under consideration in the following sense; in the frame of the formalism used in this work the usual Tikhonov regularization[35, 38, 39] widely applied to solve the integral adsorption equation (see refs. 15, 44, etc.) can be interpreted as the following minimization problem

$$\text{minimize}\left\{V_{\bar{n}(n)}^2\left(\vec{P}(\vec{B}_n) - \vec{\tilde{f}}_{\bar{n}(n)}\right) + \alpha V_n^2(\vec{B}_n)\right\}, \qquad \alpha > 0.$$

There are many versions of this algorithm in the literature, but the heart of the matter is the same. This regularization is applicable only if the distribution function is square integrable, that is, if satisfies

$$\int_0^{\infty} N(E)^2 \, dE < \infty,$$

but it is impossible to derive this condition from the physical hypothesis we have at our disposal. The only physical condition we have is

$$\int_0^{\infty} N(E) \, dE = 1$$

and this is the only one we use in our regularization procedure.

Below, we present numerical examples to demonstrate that the Tikhonov regularization applied to problems with nonsquare integrable energy distributions gives erroneous results.

Numerical Algorithms

Let w_l, $l = \overline{0, n-1}$, be real and Ψ_l, $l = \overline{0, n-1}$, be imaginary. (If $\Psi_l = \Psi(w_l)$ and w_l is real, then Ψ_l is automatically imaginary.) We shall consider only three cases: $m = 1, 2, \infty$. In these cases it is possible to solve the minimization problem using linear programming or linear-quadratic programming techniques. In the sequel $n' \le n$, where n' is the degree of the polynomial approximation and n is the number of "experimental" points. In the case $m = 1$, the minimization problem [eq. (21)] has the form

$$\begin{aligned} &\sum_{l=0}^{n-1} \left| \frac{1}{2} \sum_{k=0}^{n'-1} B_k w_l^k - i\Psi_l \right| \to \min, \\ &|B_k| \le \frac{1}{\pi}, \qquad k = \overline{0, n'-1}. \end{aligned} \tag{22}$$

It can be reduced to a linear programming problem. Indeed, introducing new variables v_l, $l = \overline{0, n-1}$, we obtain

$$\sum_{l=0}^{n-1} v_l \to \min,$$

$$v_l \ge \frac{1}{2} \sum_{k=0}^{n'-1} B_k w_l^k - i\Psi_l, \qquad l = \overline{0, n-1},$$

$$v_l \ge -\frac{1}{2} \sum_{k=0}^{n'-1} B_k w_l^k + i\Psi_l, \qquad l = \overline{0, n-1},$$

$$B_k \le \frac{1}{\pi}, \qquad k = \overline{0, n'-1},$$

$$B_k \ge -\frac{1}{\pi}, \qquad k = \overline{0, n'-1}.$$

Consider now $m = \infty$. Then the minimization problem [Eq. (21)] has the form

$$\begin{aligned} &\max_{l=\overline{0,n'-1}} \left| \frac{1}{2} \sum_{k=0}^{n-1} B_k w_l^k - i\Psi_l \right| \to \min, \\ &|B_k| \le \frac{1}{\pi}, \qquad k = \overline{0, n'-1}. \end{aligned}$$

It can be reduced to a linear programming problem introducing a new variable v:

$$v \to \min,$$

$$v \ge \frac{1}{2} \sum_{k=0}^{n'-1} B_k w_l^k - i\Psi_l, \qquad l = \overline{0, n-1},$$

$$v \ge -\frac{1}{2} \sum_{k=0}^{n'-1} B_k w_l^k + i\Psi_l, \qquad l = \overline{0, n-1},$$

$$B_k \le \frac{1}{\pi}, \qquad k = \overline{0, n'-1},$$

$$B_k \ge -\frac{1}{\pi}, \qquad k = \overline{0, n'-1}.$$

These two problems can be solved using the simplex method or interior-point techniques.[45]

Finally, for $m = 2$, we have a linear-quadratic programming problem

$$\begin{aligned} &\sum_{l=0}^{n-1} \left| \frac{1}{2} \sum_{k=0}^{n'-1} B_k w_l^k - i\Psi_l \right|^2 \to \min, \\ &|B_k| \le \frac{1}{\pi}, \qquad k = \overline{0, n'-1}. \end{aligned}$$

The Tikhonov regularization method takes the form

$$\sum_{l=0}^{n-1} \left| \frac{1}{2} \sum_{k=0}^{n'-1} B_k w_l^k - i\Psi_l \right|^2 + \alpha \sum_{k=0}^{n'-1} B_k^2 \to \min, \tag{23}$$

where $\alpha > 0$ is a regularization parameter.

Numerical Experiments

Here, we present some results of numerical experiments with distribution functions of different types. As we have already mentioned the Tikhonov regularization is applicable only if the distribution function is square integrable. In this case the two regularization methods give comparable results. We use $\rho = 0.99$ in eq. (18). All "experimental" points w_l are uniformly distributed in the interval $(-1, 1)$.

Consider the function

$$N(E) = 0.56419 \cdot \exp\bigl(-(E-4)\bigr)^2.$$

The adsorption isotherm is "measured" at 49 points, with random errors of 1%. The distribution function is reconstructed using polynomials of 10th degree. The results are presented in Figures 1–3.

The distribution N is shown by dashed line, and the reconstructed distribution is shown by solid line. In Figure 1, the reconstruction is done solving the minimization problem [eq. (23)] with the regularization parameter $\alpha = 0$. Figure 2 shows the results of reconstruction by the same method with the regularization parameter $\alpha = 0.001$. The reconstruction using the method [eq. (22)] is shown in Figure 3.

Now we present an example of another type. Consider the function

$$\phi(t) = \begin{cases} 0, & t \in [0, 1/2], \\ A(|1-t|^{-1/2} - \sqrt{2}), & t \in (1/2, 1) \cup (1, 3/2), \\ 0, & t \in [3/2, \infty), \end{cases}$$

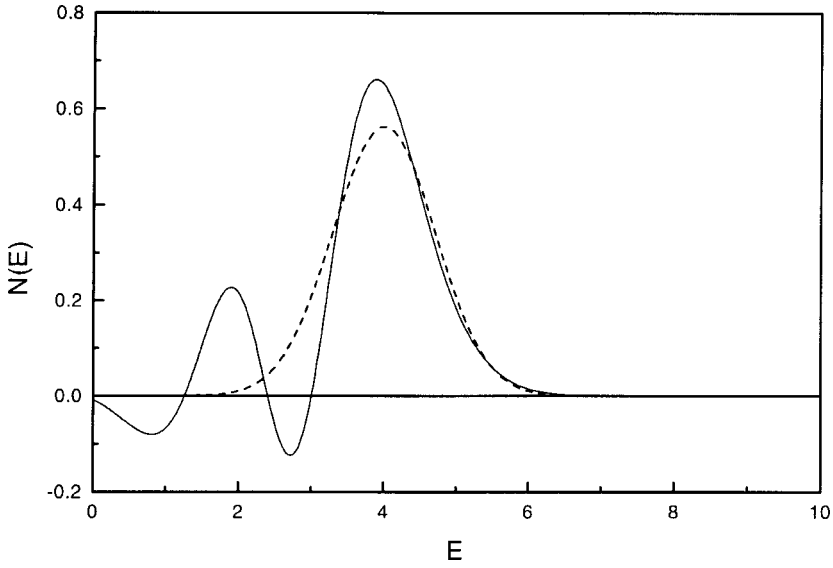

FIGURE 1. Reconstruction of the gaussian energy distribution by the method [eq. (23)] with $\alpha = 0$. The postulated distribution is shown by a dashed line, the reconstructed distribution is shown by a solid line.

where

$$A = \left(\ln \frac{\sqrt{2}+1}{\sqrt{2}-1} - \sqrt{2} \ln 3 + 2 \arctan \frac{1}{\sqrt{2}} \right)^{-1}.$$

Then $\Phi(\xi)$, defined by eq. (9), can be easily evaluated:

$$\Phi(\xi) = \frac{A}{\sqrt{1+\xi}} \left(\ln \frac{\sqrt{2(1+\xi)}+1}{\sqrt{2(1+\xi)}-1} + 2 \arctan \frac{1}{\sqrt{2(1+\xi)}} \right) - \sqrt{2} A \ln \frac{3+2\xi}{1+2\xi}. \quad (24)$$

Obviously, $\Phi(0) = 1$. The function ϕ is not square integrable, and in this example the Tikhonov regularization can cause serious reconstruction errors.

The distribution N corresponding to the function Φ is "measured" at 45 points, with random errors of 1%. Using polynomials of 10th degree the distribution N is reconstructed. The results are presented in Figures 4–6. The distribution N is shown by dashed line, and the reconstructed dis-

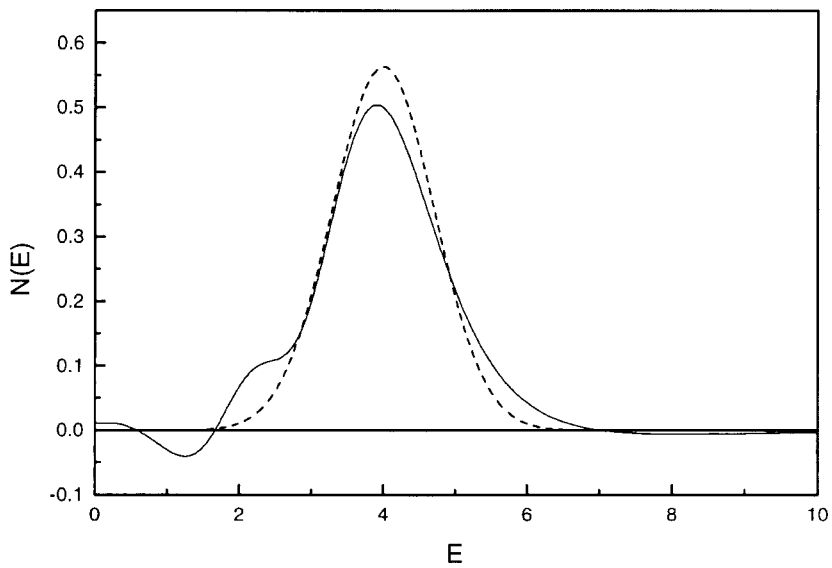

FIGURE 2. Reconstruction of the gaussian energy distribution by the method [eq. (23)] with $\alpha = 0.001$. The postulated distribution is shown by a dashed line, the reconstructed distribution is shown by a solid line.

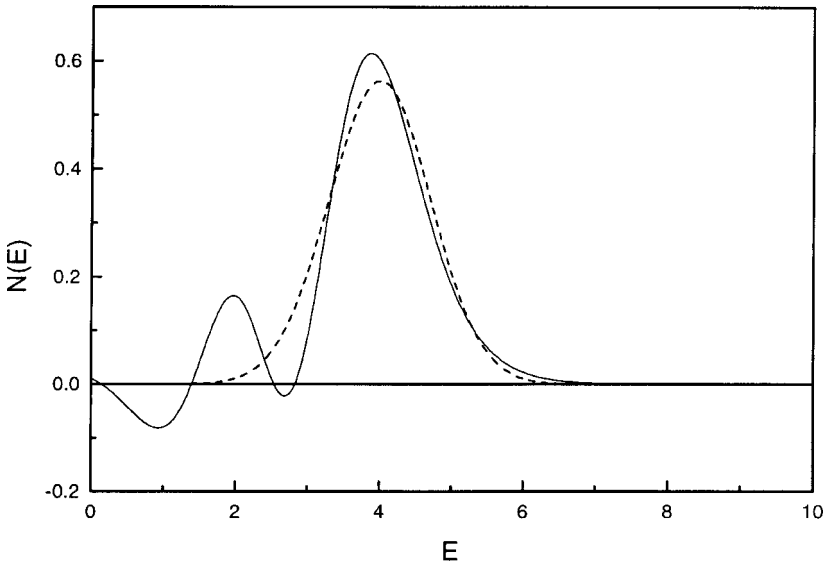

FIGURE 3. Reconstruction of the gaussian energy distribution by the method [eq. (22)]. The postulated distribution is shown by a dashed line, the reconstructed distribution is shown by a solid line.

tribution is shown by solid line. In Figure 4 the reconstruction is fulfilled solving minimization problem [eq. (23)] with the regularization parameter $\alpha = 0$. Figure 5 shows the results of reconstruction by the same method with the regularization parameter $\alpha = 0.001$. Finally, the reconstruction by method [eq. (22)] is shown in Figure 6.

We see that with $\alpha = 0$, the method [eq. (23)] cannot reconstruct the distribution because of measurement and computational errors. Using the regularization parameter $\alpha > 0$, we cannot identify the peak because the distribution is not square integrable, and the regularization term is too big. Our regularization even in this case gives an acceptable result.

Conclusions

In this work a new method for solving the Stieltjes integral equation is developed. Its mathematical

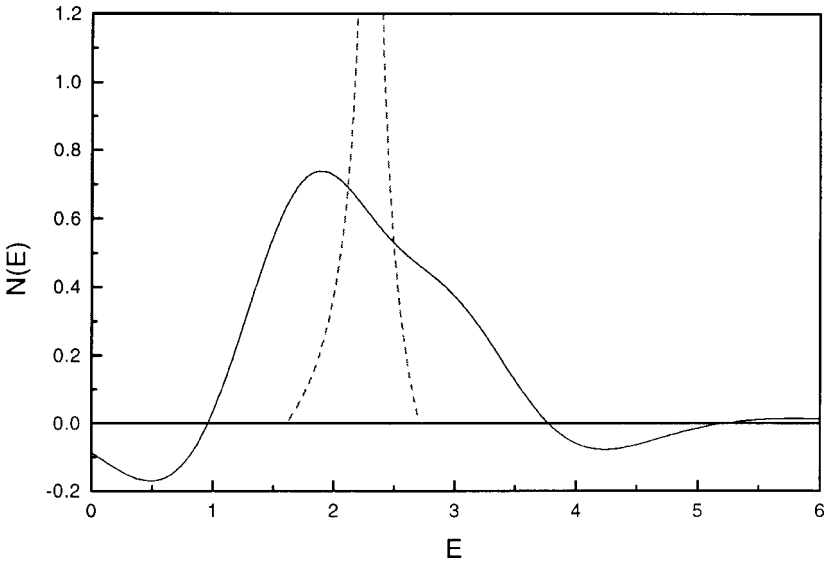

FIGURE 4. Reconstruction of the distribution with a narrow "peak" by the method [eq. (23)] with $\alpha = 0$. The postulated distribution is shown by a dashed line, the reconstructed distribution is shown by a solid line.

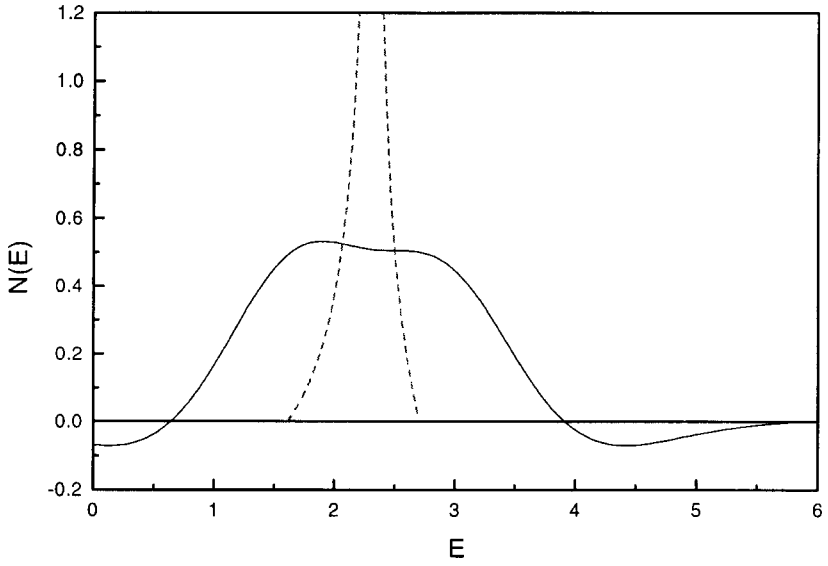

FIGURE 5. Reconstruction of the distribution with a narrow "peak" by the method [eq. (23)] with $\alpha = 0.001$. The postulated distribution is shown by a dashed line, the reconstructed distribution is shown by a solid line.

correctness is derived only from natural physical assumptions. Computationally, the method allows reduction of the original problem to a linear programming or quadratic programming problem that can be solved by the well-known simplex method or by an interior-point algorithm.

The method is compared with the usually applied Tikhonov regularization method. Our numerical experiments show that in the case of a distribution with a relatively small L_2-norm the both methods give close results, and in the case of a distribution with a big L_2-norm the Tikhonov regularization does not work, while our algorithm gives an acceptable reconstruction. We face distributions with a big L_2-norms, for example, in the case of an almost homogeneous surface. The distribution corresponding to such surface has the form of a narrow "peak." For some surfaces the distribution can also be composed of one or several narrow "peaks" and some broad low "hills." The information con-

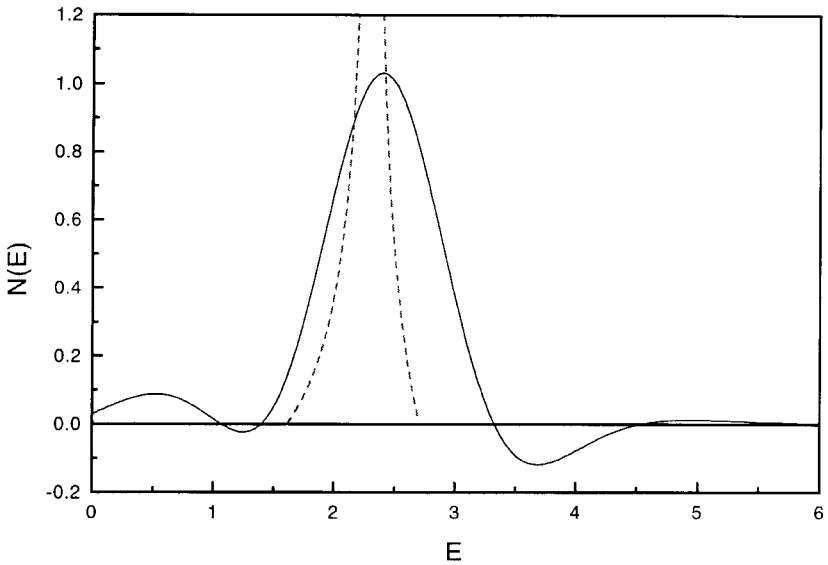

FIGURE 6. Reconstruction of the distribution with a narrow "peak" by the method [eq. (22)]. The postulated distribution is shown by a dashed line, the reconstructed distribution is shown by a solid line.

cerning the structure of the distribution is not *a priori* known, and a correct reconstruction of narrow "peaks" is of importance. The proposed method solves this problem, and seems to be a promising tool for the experimental data analysis. We hope that this new approach will be a useful complement to the existing reconstruction techniques.

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